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(54) Manufacturing process for grooved substrates and multilayer structure.

(57) Grooved substrates and multilayer structures, especially suitable for optical disks, are taught. The major process steps include spin coating of a supporting plate (1) with dissolved material forming a soft layer (7) thereon, stamping grooves (2) into the soft layer (7) to form a structured soft layer showing the negative image of the stamp and hardening the structured soft layer (7) by thermal treatment. The dissolved material contains polymeric organometal compounds comprising polymer siloxane and/or polymer silicates. In one embodiment the structured soft layer is a dielectric layer (8) containing various combinations of the oxides SiO_2 , La_2O_3 , PbO and TiO_2 . The multilayer structure is completed by a magneto-optic layer (4), a reflector layer (5) and a passivation layer (6).

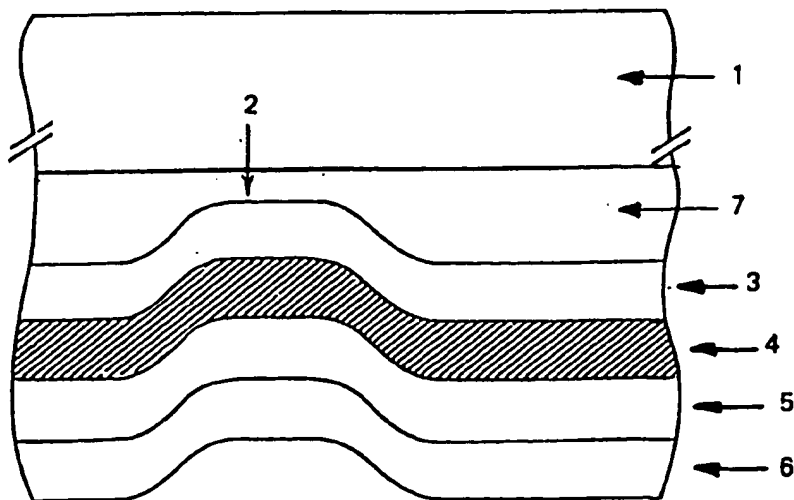


FIG. 3A

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The present invention relates to a process for manufacturing a grooved substrate and to a multilayer structure. The grooved substrate and the multilayer structure are especially suitable for optical disks.

Microstructuring of thin dielectric layers or processes for manufacturing grooved substrates are needed in the whole data processing technology. Applications are to be found not only in the semiconductor and packaging technology but also in integrated optics technology, in the storage technology, e.g. for data communications, for magnetic disks and especially for optical disks. The high storage density of optical disks is achieved by using beam diameters of approximately 1 μm . The information is recorded at a predetermined position and read out from a predetermined position. Therefore the beam position needs to be accurately controlled by the use of guide addresses or guide signals. These typically are microscopic grooves, which in conjunction with a sensing mechanism and a servo system operating upon the optical beam serve to guide the beam in the correct direction during recording and reading operations. Various methods for forming the grooves on the optical disk have been proposed.

PCT/EP88/00479 describes a hot stamping process for forming the tracking grooves directly in the glass surface of an optical disk. According to this method the glass substrate is heated in excess of the softening point of the glass types used, typically higher than 600 °C. The temperature of the heated stamp should preferably be lower than the transformation temperature of the glass type used, typically 380 - 450 °C. The microstructure on the heated stamper deforms the surface of the glass substrate resulting in a corresponding microstructure on the surface of the glass substrate, which, when separated from the stamper and cooled in a controlled manner, gives the desired surface microstructure on the glass substrate. Microstructures formed on the surface of the glass substrate using the hot stamping process as described above conform to the microstructure on the stamper across the area of the substrate surface, but, for example, the glass may flow into a deep groove in the stamper to give a shallow protrusion on the substrate surface. Since for reasons of economy and product cost reduction it is desired to re-use the stamper a number of times the hot stamping process needs the selection of appropriate stamping conditions and coating materials for the glass layer to enable a single stamper to be used repeatedly without sticking problems. The high temperatures applied to the glass substrate during hot stamping processes, e.g. higher than 600 °C, may cause the deformation of the glass substrate.

The method for manufacturing substrates having a large number of fine grooves thereon as described in US-A-4 810 547 comprises applying a solution containing at least one organometal compound and a thickening agent onto a body of substrate to form a film having plasticity, impressing in the surface of the film formed on the substrate with a mold and calcining the film to solidify the same. A similar method is claimed in the unexamined Japanese patent application JP 62 102 445.

These methods provide advantages in that the resulting film has a shrinkage lower than that of gel films as for example used in PCT/GB88/01080 and seldom causes cracks and/or warpage due to nonuniform drying rate since the organometal compound is formed in a film on the substrate body.

When used for optical disks grooved substrates and structures should have a high refractive index and a high signal to noise ratio in addition to the already mentioned properties. This normally is achieved by producing a multilayer structure on a grooved substrate, as described by Takahashi et al. in "High quality magneto-optical disk", SPIE Vol.695 Optical Mass Data Storage II (1986).

There has been a strong need for substrates with fine grooves, especially for optical disks, which do not show the various disadvantages afore mentioned and which, on the contrary, have an extremely high dimensional stability and reliability as well as a high productivity in their manufacturing process. Thus it is a principal object of the present invention to provide a new grooved substrate with extremely high dimensional stability, sharp edges of the grooves and exact transfer of the stamper image to the substrate.

Another major object of the present invention is to enhance the refractive index and the signal to noise ratio of the grooved substrate especially when used for optical disks.

It is another object of the present invention to avoid blisters or cracks in the grooved film.

A further object of the present invention is to provide a manufacturing process which ensures the re-use of the stamper and which is quite simple and economic.

The above mentioned and other objects of the present invention are achieved by providing a multilayer structure comprising a substrate with plane, unstructured surfaces, a structured glasslike layer provided on one surface of said substrate, wherein said glasslike layer contains grooves in the layer surface not adjacent to said substrate, a dielectric layer disposed on said structured glasslike layer, a magneto-optic layer disposed on said dielectric layer, a reflector layer disposed on said magneto-optic layer and a passivation layer disposed on said reflector layer, wherein said dielectric layer, said magneto-optic layer, said reflector layer and possibly said passivation layer contain the grooves of said structured glasslike layer.

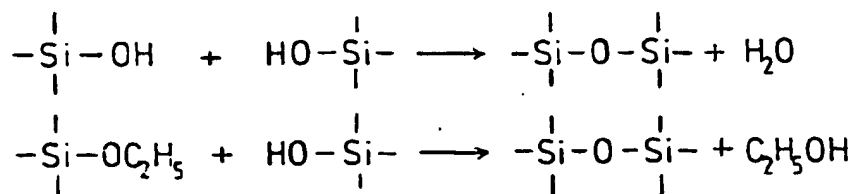
This multilayer structure and other grooved substrates may be manufactured according to a process comprising the steps of spin coating of a supporting plate with dissolved material, forming a soft layer on

said supporting plate, stamping grooves into said soft layer with a stamp, wherein said stamp shows the negative image of the structure to be transmitted to said soft layer thus forming a structured soft layer, hardening of said structured soft layer to transform said structured soft layer into a hard, structured layer, wherein said hardening is accomplished by thermal treatment, wherein said dissolved material contains at least one polymeric organometal compound.

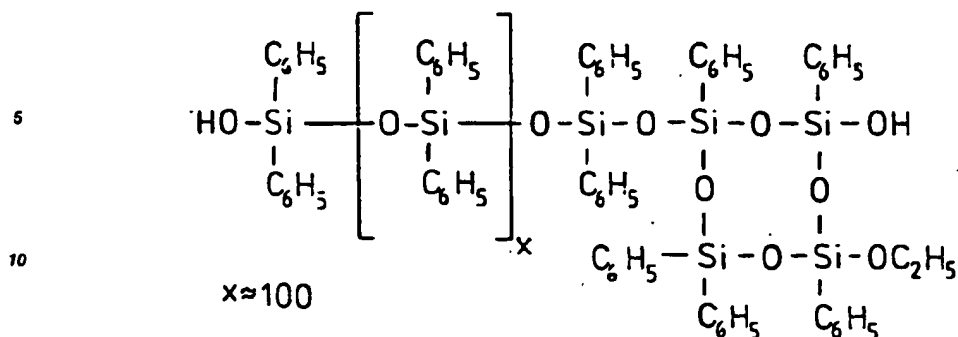
Further developments are laid down in subclaims 2 to 7. Ways of carrying out the invention are described in more detail below with reference to the drawing which illustrates only specific embodiments and in which

- Fig. 1A shows a part of the surface of an embodiment of a grooved substrate with a magnification factor of 5000;
 Fig. 1B shows a part of the surface of the same embodiment; due to a magnification factor of 20.000 the fine grooves with their sharp edges may be seen;
 Fig. 1C and Fig. 1D show both a part of the surface of an embodiment with a magnification factor of 10.000;
 Fig. 2 is a schematic diagram showing the cross-section of a state of the art grooved structure for optical disks;
 Fig. 3A is a schematic diagram showing the cross-section of one embodiment of the present invention;
 Fig. 3B is the same diagram as in Fig. 3A showing another embodiment,
 Fig. 3C is a schematic diagram showing the cross-section of one embodiment with two multilayer structures attached to each other and
 Fig. 4 is a diagram explaining the enhancement of signal-to-noise ratio and refractive index dependent on the dielectric layer thickness.

Referring now to Figs. 1A and 1B the surface of a grooved substrate with stamped fine grooves of 1 μm in width and 70 nm in depth with their sharp edges are clearly to be seen. To produce a substrate with fine grooves a supporting plate is spin-coated with dissolved material forming a soft layer on the supporting plate. The dissolved material contains controlling compounds and polymeric organometal compounds. The controlling compounds control the viscosity of the layer during the following process steps. Especially the spin-on time, the number of revolutions per minute during the spin-on step, the transportation time to the stamp and the time delay until the stamping step is carried out are to be adjusted carefully. The controlling compounds comprise ethylene glycol. Grooves are stamped in the soft layer with a stamp showing the negative image of the structure to be transmitted to the soft layer. By thermal treatment the structured layer is hardened and transformed into a hard structured layer. In accordance with the invention the polymeric organometal compounds comprise polymer siloxane $[\text{R}_x\text{SiO}_y]_n$ or silsesquioxane, polymeric titanate $[\text{TiO}_2]_n$ and polymer silicates $[\text{SiO}_2]_n$ like phosphosilicates or phosphosiloxane. These materials consist of long molecule chains containing reactive silanol groups with a high silicon portion. During the hardening step the soft structured layer is transformed into a hard, SiO_2 -like layer. This transformation takes place accompanied by volume reduction due to polycondensation and thermodegradation effects:



Typical condensation reaction



Typical structure of polymer siloxane network

The use of dissolved material containing already polymerized organometal compounds with a high Si content decreases the volume reduction considerably. This effect may be intensified by lowering the portion of solvent in the controlling compounds. By carefully choosing the amount of solvent the drying speed of the spun-on dissolved material is controlled. A high moisture content of the soft layer to be structured will cause the destruction of the grooved structure during the separation of the stamp. Using an ethylene glycol portion of about 30% results in a drying speed reduction without affecting the accurateness of the replication. Similar solvents like glycerine also reduce the drying speed but cause micro bubbles in the structured layer leading to poorly defined edges. With a thermo gravimetric analysis information about the weight loss of the organometal compounds during the hardening Step may be obtained. The weight loss depends on the hardening temperature and the atmosphere. ACCUGLASS 204 (trademark of Allied-Signal Inc., Milpitas, CA), containing polymer siloxane as organometal compound, shows a continuous weight loss in the temperature range from 50 °C to about 480 °C. In air the weight loss is as small as about 13% and in nitrogen atmosphere it is even lower with about 7%. Very low weight losses are shown by ACCUGLASS x11 series with 5% (+/- 1 %). Thus the process as claimed leads to less volume shrinkage and thus higher exactness in accepting and keeping the form of the stamp, resulting in grooved substrates with extremely high dimensional stability, sharp edges of the grooves and exact transfer of the stamper image to the substrate, avoiding blisters or cracks in the grooved film.

The stamping is carried out at room temperature and at low stamping pressure, preferably at about 1 to 6 bar in an isobaric press. These conditions avoid breakage of the stamper plate by foreign particles and the deformation of the microstructure of the stamper. The stamp is preferably coated with a thin carbon layer of preferably about 0.4 µm to prevent it from sticking to the structured soft layer. Other coating materials tested like silicon, siliconoxide, siliconnitride, nickel or tungsten lead to a close sticking of the stamp to the structured soft layer. The typical adhesion shown by the plane and parallel surfaces of the stamp and the structured layer in intimate contact after the stamping step may be overcome by a special treatment without applying external forces. Heating up the stamp to about 130 °C assures the uniform detachment of the stamp and the integrity of the grooved structures as well as of the stamp itself. During this thermal treatment small amounts of solvent of the structured layer evaporize forming a sort of gaseous bolster between the coated stamp and the structured layer. This detachment mechanism is supported by the different thermal expansion coefficients of the coated stamp and the structured layer. Thus after, if necessary, a simple cleaning procedure the stamp may be reused leading to a considerable reduction of the manufacturing costs.

To achieve grooves of 1 µm in width and 70nm in depth a mixture of 1 g ethylene glycol and 30 g Accuglass 204 is spun on the cleaned glass substrate within 10 s at 1500 rpm. At a stamping pressure of about 6 bar the desired structure is stamped into the spun-on layer with a carbon coated stamp within 3 minutes. Then the structured layer and the stamp adhering to it are heated up to about 130 °C. After

approximately 4 to 5 minutes the stamp detaches from the grooved substrate more or less automatically, it pops up, without applying external forces. The following thermal treatment at about 400 °C during about 1 hour transforms the structured soft layer into a hard, transparent layer showing good adhesion to the glass substrate underneath. In another experiment a mixture of 1g ethylene glycol and 30g ACCUGLASS 310 is spun on the glass substrate within 70s at 1500 rpm and stamping is carried out at a stamping pressure of 3 bar within 2.5 minutes. Excellent results were obtained showing very fine grooves in the hardened structured layer with widths of 0.4 µm and below.

Fig. 1C and Fig. 1D show both a part of the surface of an embodiment. In Fig. 1C the grooves have been stamped after air drying of the spun-on soft layer. In Fig. 1D a prebake and cure step were applied to the soft layer after the stamping step. There can be seen no difference in the sharpness of the grooves of Fig. 1C and Fig. 1D. Due to the high Si content in the polymerized organometal compounds of the dissolved material forming the soft layer this layer already shows a high dimensional stability before the thermal treatment of the hardening step. The volume shrinkage of the structured soft layer thus is low and this leads to a high exactness of the stamper image shown by the grooved film.

Fig. 2 is a schematic diagram showing the cross-section of a state of the art grooved structure for optical disks. The grooves 2 are provided in the substrate 1 itself and the layers forming the complete structure are disposed on the grooved substrate. These four layers consist of a dielectric layer 3 of about 50 nm, thickness, a magneto-optic layer 4 of about 35 nm thickness, a reflector layer 5 of about 60 nm thickness and a passivation layer 6 of about 100 nm thickness.

Fig. 3A is a schematic diagram showing the cross-section of one embodiment of the present invention. In this embodiment a silicon dioxide layer 7 is disposed on the plane surface of the unstructured substrate 1 and the grooves 2 are provided in the surface of the silicon dioxide layer 7 not adjacent to the unstructured substrate 1. The four layers completing the structure are disposed on the grooved silicon dioxide layer 7. Four layers are provided with the same specification and in the same sequence as described above in connection with Fig. 2.

Fig. 3B is the same diagram as in Fig. 3A showing another embodiment in which a dielectric layer 8 is disposed on the plane surface of an unstructured substrate 11. The grooves 2 are provided in the surface of the dielectric layer 8 not adjacent to the unstructured substrate 11. The dielectric layer 8 contains various combinations of the oxides SiO₂, La₂O₃, PbO and TiO₂ and replaces the dielectric layer structure of the embodiment of Fig. 3A consisting of a SiO₂-layer and an AlN-layer.

The refractive index D and the signal-to-noise ratio (SNR) of the structure are enhanced in dependence of the thickness d of the dielectric layer. This is of special importance when the structure is used for optical disks. Receiving these results with only one dielectric layer using the above described composition additionally reduces the complexity of the manufacturing process and the process costs.

Three layers, a magneto-optic layer 4, a reflector layer 5 and a passivation layer 6 are completing the structure and are disposed on the grooved dielectric layer 8. These three layers have the same specification and are disposed in the same sequence as described above in connection with Fig. 2.

Fig. 3C shows the cross-section of an embodiment with two multilayer structures attached to each other, e.g. by glueing, allowing at the same time the use of both sides of the structure to read or write information. An adhesive layer 9 sandwiched between protective layers 10 links the two multilayer structures.

The enhancement of the signal-to-noise ratio and the refractive index in dependence of the thickness of the dielectric layer is shown in Fig. 4 published in "Antireflection Structures for Magneto-Optic Recording", OSA Technical Digest Series, Vol.10, p.138-9, 1987. The grooves in the embodiments described in Fig. 3A and 3B may be manufactured following the process steps of the invention:

Spin coating of a supporting plate (1) with dissolved material forming a soft layer (7) on said supporting plate (1), stamping grooves (2) into said soft layer with a stamp, wherein said stamp shows the negative image of the structure to be transmitted to said soft layer (7), thus forming a structured soft layer (7), hardening of said structured soft layer (7) to transform said structured soft layer (7) into a hard, structured layer (7), wherein said hardening is accomplished by thermal treatment, wherein said dissolved material further contains controlling compounds which control the viscosity of said layer during the process steps of spin coating and of stamping grooves, wherein said controlling compounds comprise ethylene glycol.

To those skilled in the art it will be obvious that this process to manufacture grooves in a substrate could equally be well adapted to other articles which have a microstructure which must be accurately formed on the surface of plate like diffraction gratings or fresnel lenses.

Claims

1. Process for manufacturing a grooved substrate especially for optical disks comprising
 - spin coating of a supporting plate (1) with dissolved material forming a soft layer (7) on said supporting plate (1)
 - 5 - stamping grooves (2) into said soft layer with a stamp wherein said stamp shows the negative image of the structure to be transmitted to said soft layer (7) thus forming a structured soft layer (7)
 - hardening of said structured soft layer (7) to transform said structured soft layer (7) into a hard structured layer (7) wherein said hardening is accomplished by thermal treatment
 - 10 characterized in that said dissolved material contains polymeric organometal compounds, wherein said organometal compounds comprise polymer siloxan and/or polymer silicates.
2. Process in accordance with claim 1 wherein said dissolved material further contains controlling compounds which control the viscosity of said layer during the process steps of spin coating and of stamping grooves, wherein said controlling compounds comprise ethylene glycol.
- 15 3. Process in accordance with claim 1 or 2 wherein said stamping is carried out at room temperature.
4. Process in accordance with anyone of the preceding claims wherein said stamping is carried out at low stamping pressure, preferably at about 6 bar.
- 20 5. Process in accordance with anyone of the preceding claims wherein said stamp is coated with a thin carbon layer which preferably has a thickness of about 0.4 μm .
- 25 6. Process in accordance with anyone of the preceding claims wherein said stamp is separated after completion of the stamping process by thermal treatment carried out at about 130° C without applying external forces.
7. Process in accordance with anyone of the preceding claims wherein said hardening by thermal treatment is carried out at about 400° C during about 1 hour.
- 30 8. Multilayer structure especially for optical disks comprising
 - a substrate (1) with plane, unstructured surfaces
 - a structured glasslike layer (7) provided on one surface of said substrate (1)
 - 35 wherein said glasslike layer (7) contains grooves (2) in the layer surface not adjacent to said substrate (1).
 - a dielectric layer (3) disposed on said structured glasslike layer (7)
 - a magneto-optic layer (4) disposed on said dielectric layer (3).
 - 40 - a reflector layer (5) disposed on said magneto-optic layer (4) and
 - a passivation layer (6) disposed on said reflector layer (5),
 - wherein said dielectric layer (3), said magneto-optic layer (4), said reflector layer (5) and possibly said passivation layer (6) contain the grooves (2) of said structured glasslike layer (7) and
 - 45 wherein said structure is preferably manufactured following the process steps in accordance with anyone of the preceding claims 1 to 7.
9. Multilayer structure especially for optical disks comprising
 - 50 - a substrate (11) with plane, unstructured, parallel surfaces
 - a structured dielectric layer (8) provided on one surface of said substrate (11)
 - wherein said dielectric layer (8) contains grooves (2) in the layer surface not adjacent to said substrate (11)
 - 55 - a magneto-optic layer (4) disposed on said dielectric layer (8)
 - a reflector layer (5) disposed on said magneto-optic layer (4) and
 - a passivation layer (6) disposed on said reflector layer (5),

wherein said magneto-optic layer (4), said reflector layer (5) and possibly said passivation layer (6) contain the grooves (2) of said structured dielectric layer (8) and

wherein said structure is preferably manufactured following the process steps in accordance with anyone of the preceding claims 1 to 7.

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10. Multilayer structure especially for optical disks in accordance with claim 9 wherein said structured dielectric layer (8) contains various combinations of the oxides SiO_2 , La_2O_3 , PbO and TiO_2 , preferably SiO_2 , La_2O_3 and PbO .

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11. Multilayer structure especially for optical disks in accordance with anyone of claims 8 to 10 wherein said magneto-optic layer (4) is made of materials comprising mixtures of rare earth elements and transition elements like TbFeCo , TbFe , GdFe , TbGdFe , GdTbCo , TbFeCo , NdFeCo or NdTbFeCo , said reflector layer (5) contains Al , Cr , Ag or Au and said passivation layer (6) contains one or more components out of the group of AlN , SiO_2 , ZrO_2 , Al_2O_3 , TiO_2 , TaO_2 and Si_3N_4 .

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12. Multilayer structure especially for optical disks comprising two multilayer structures in accordance with claim 8 or 9 wherein said two multilayer structures are attached to each other.

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13. Optical storage system characterized in that said optical storage system contains a multilayer structure as set forth in one or more of the claims 8 to 12.

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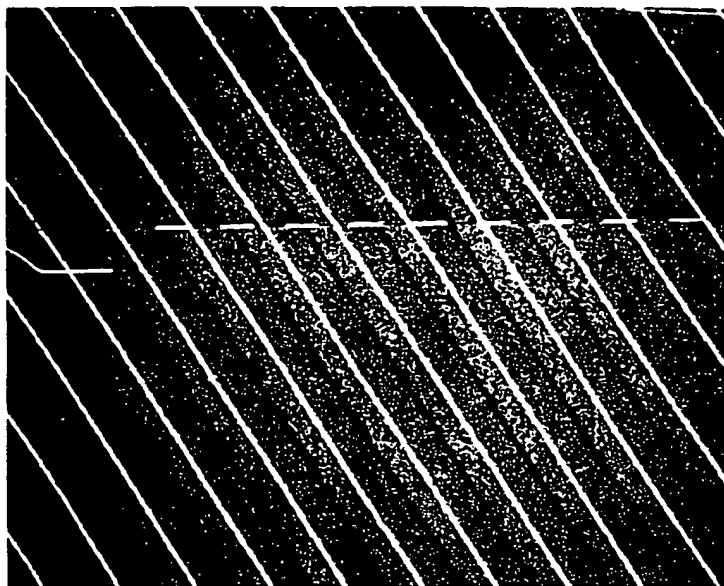


FIG. 1A

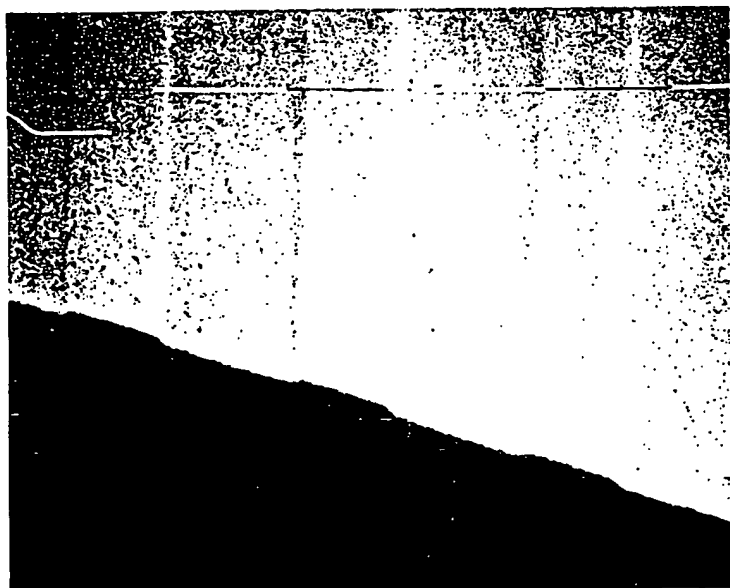
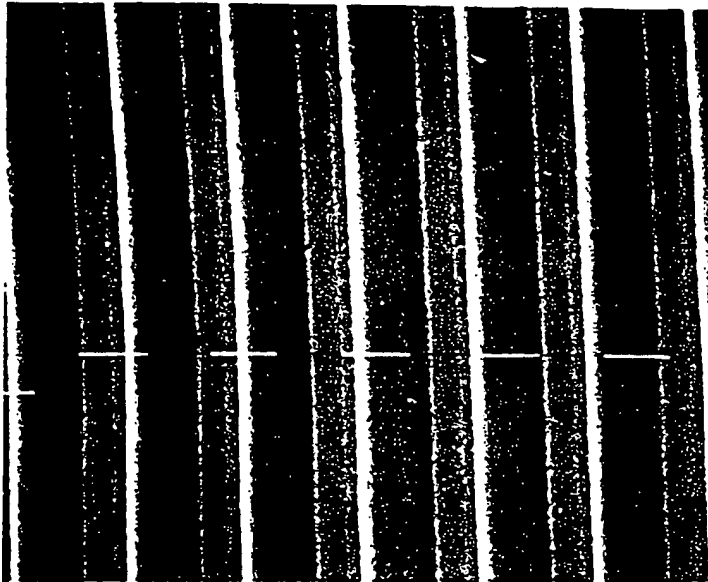
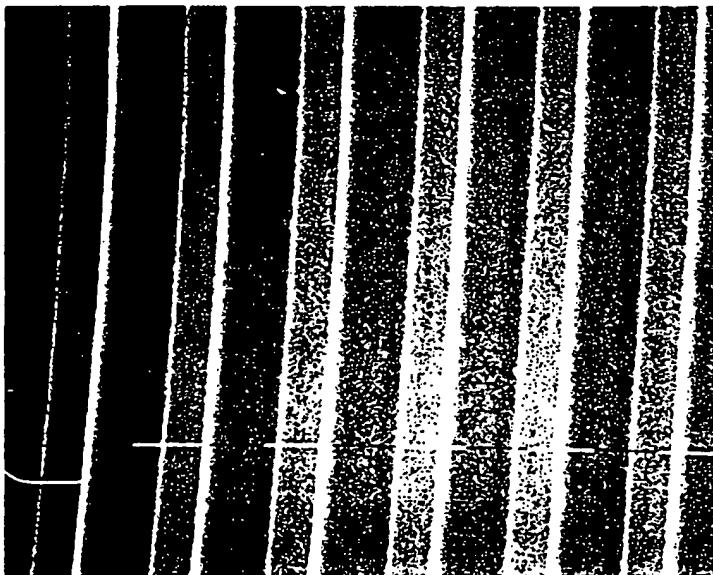


FIG. 1B



FRESHLY
PRESSED

FIG. 1C



ADDITIONALLY
PREBAKED
AND CURED

FIG. 1D

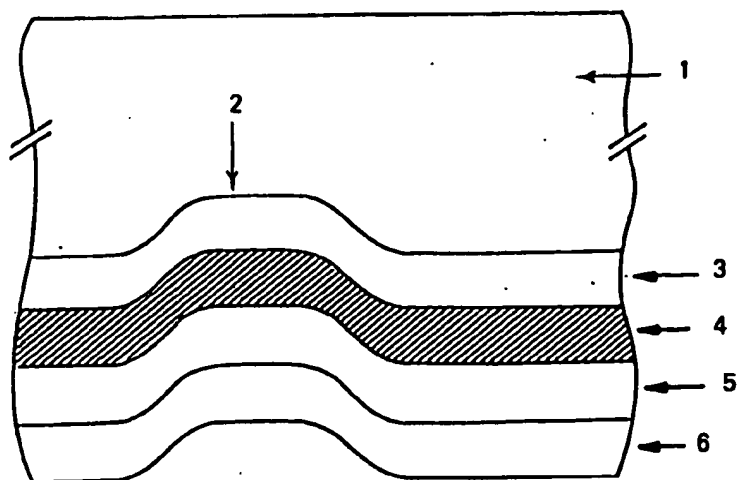


FIG. 2

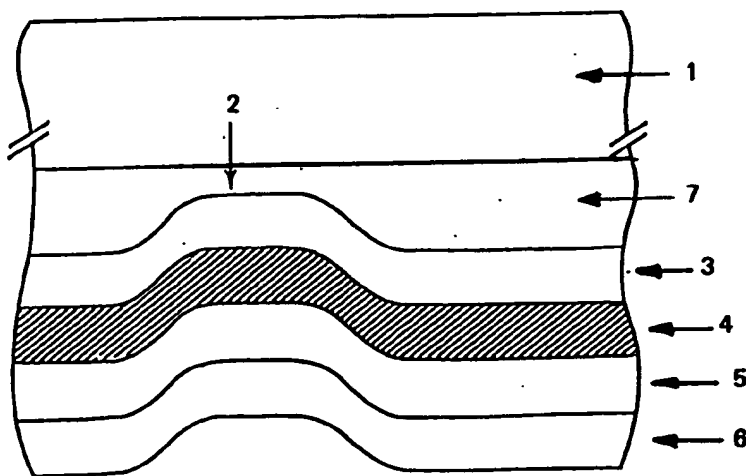


FIG. 3A

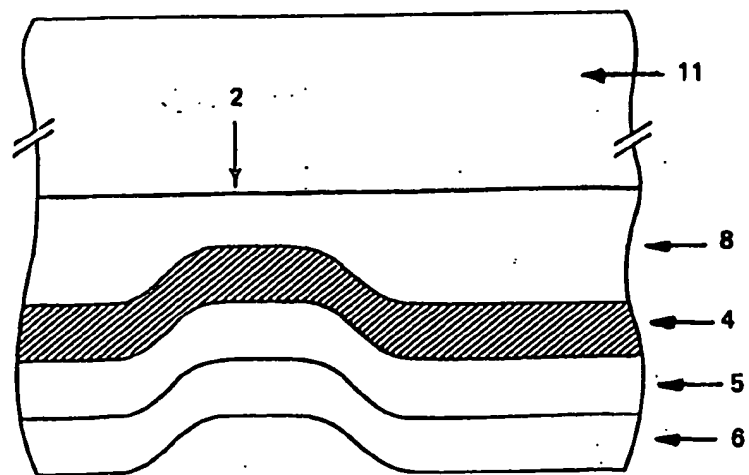


FIG. 3B

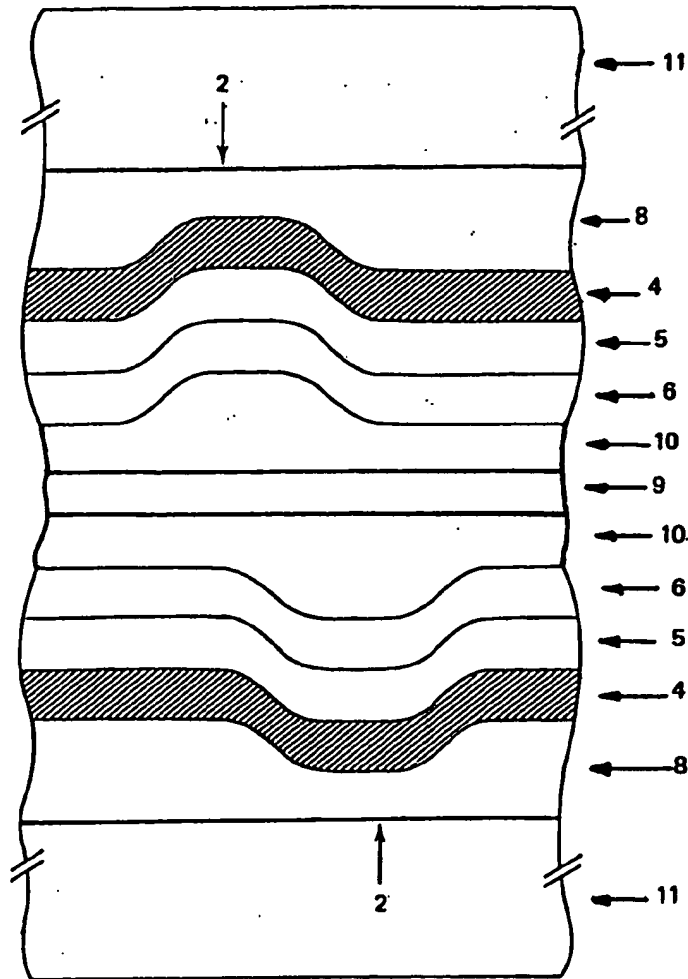


FIG. 3C

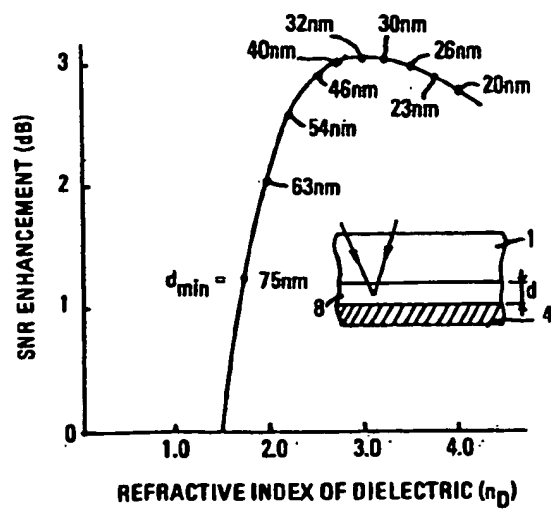


FIG. 4



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 90 11 5758

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	US-A-4 810 547 (MINAMI et al.) * The whole document * -----	1-7	G 11 B 7/26 B 29 D 17/00
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G 11 B B 29 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10-05-1991	Examiner BENFIELD A.D.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons Δ : member of the same patent family, corresponding document			



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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid,
namely claims:
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

X LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,
namely:

See sheet -B-

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid,
namely claims:
- ☒ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims,
namely claims: 1-7



European Patent
Office

EP 90 11 5758 -2-

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims 1-7: Process for manufacturing an substrate.
2. Claims 10-12: Multi-layer recording medium.
3. Claims 13: Optical recording process.